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(54) Etching composition and use

(57) An aqueous etchant composition containing about 0.01 to about 15 percent by weight of sulphuric acid and about .01 to about 20 percent by weight of hydrogen peroxide or about 1 to 30 ppm of ozone, and about 0.01 to 100 ppm of hydrofluoric acid is effective in removing polymer and via residue from a substrate or conductive material, and especially from an integrated circuit chip having aluminum lines thereon.

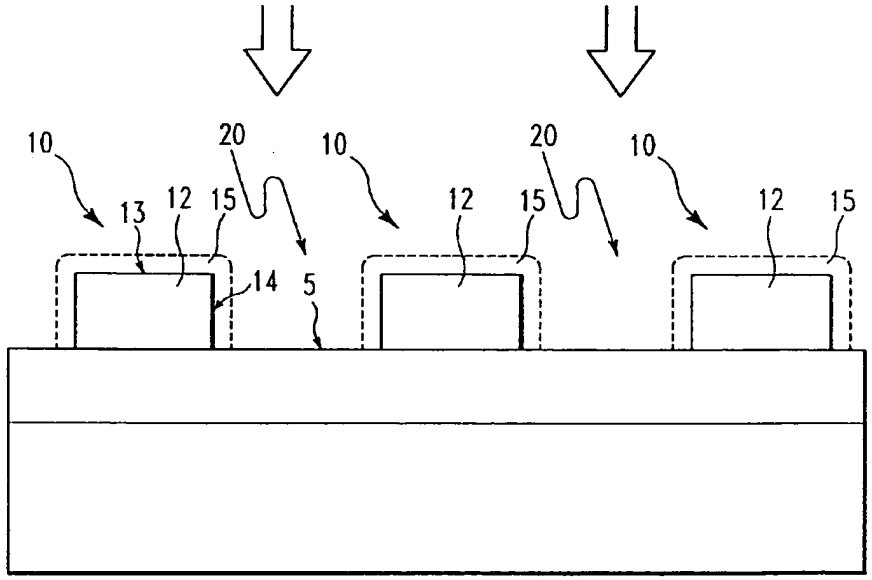

FIG. 1

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the following detailed description of the invention, in which:

[0010] Figure 1 is a cross-sectional view of a portion of a semiconductor device illustrating a problem the instant invention is seeking to solve.

[0011] Figure 2 is a cross-sectional view of a portion of a semiconductor device illustrating a problem the instant invention is seeking to solve.

[0012] The present invention provides an etchant composition that is capable of removing via residue and does not adversely effect the aluminum lines or lines made of other conductive materials. Moreover, the etching composition of the present invention is quite acceptable from an environmental point of view. Additionally, the etchant composition is particularly useful in removing inorganic polymers attached to the metal lines in isolated regions where there may be a higher silicon concentration as compared to the array regions.

[0013] The etchant composition of the present invention is an aqueous solution containing about 0.01 to about 15 percent by weight of sulphuric acid, about 0.01 to about 20 percent by weight of hydrogen peroxide, or about 1 to about 30 ppm of ozone, and about 0.1 to about 100 ppm of a fluoride containing compound, preferably hydrofluoric acid.

[0014] Another aspect of the present invention is concerned with removing polymer and via residue from a substrate which comprises contacting the substrate with an aqueous solution containing about 0.01 to about 15 percent by weight of sulphuric acid, and about 0.01 to about 20 percent by weight of hydrogen peroxide, or about 1 to about 30 ppm of ozone, and about 0.1 to about 100 ppm of a fluoride containing compound, preferably hydrofluic acid.

[0015] Still other objects and advantages of the present invention will become readily apparent to those skilled in this art from the following detailed description, wherein it is shown and described only the preferred embodiments of the invention, simply by way of illustration of the best mode contemplated of carrying out the invention. As will be realized, the invention is capable of other and different embodiments, and its several details are capable of modifications in various obvious respects, without departing from the invention. Accordingly, the description is to be regarded as illustrative in nature and not as restrictive.

[0016] The etchant compositions of the present invention are aqueous solutions containing about 0.01 to about 15 percent by weight and preferably about 1 to about 10 percent by weight of sulphuric acid and about 0.01 to about 20 percent by weight of hydrogen peroxide, 0.1 to about 100 ppm of hydrofluoric acid and preferably about 1 to about 10 percent by weight of hydrogen peroxide or about 1 to about 30 ppm and preferably about 5 to about 20 ppm of ozone with the balance being substantially water, and more preferably contain about 0.1 to about 100 ppm of a fluoride containing compound, preferably hydrofluoric acid. It is not necessary that the fluoride containing compound be hydrofluoric acid. It is necessary that the fluoride containing compound contribute free fluoride to the etchant composition. It is preferred that the fluoride containing compound be able to contribute the equivalent of at least about 8 and at most about 12 ppm of hydrofluoric acid to the etchant solution. A preferred composition of the present invention is an aqueous solution of about 8 percent by weight of sulphuric acid, and about 1.5 percent by weight of hydrogen peroxide and the remainder being substantially water, and more preferably contain about 10 ppm of a fluoride containing compound, preferably hydrofluoric acid. This composition is preferably employed at temperatures of about 35°C. Another more preferred composition of the present invention is an aqueous solution of about 9 percent by weight sulphuric acid and about 4 percent by weight hydrogen peroxide and the remainder being substantially water, and more preferably contain about 10 ppm of a fluoride containing compound, preferably hydrofluoric acid. This composition is preferably employed at temperatures of about 35°C and is especially preferred for removing thicker and more tenacious sidewall polymer. Yet another more preferred composition of the present invention is an aqueous solution of about 5% by weight of sulphuric acid, about 12% by weight of hydrogen peroxide and about 10 ppm hydrogen fluoride. The water employed is preferably deionized water.

[0017] These etchant compositions of the present invention can be prepared by admixing an aqueous sulphuric acid such as a 98 percent by weight solution with an aqueous solution of hydrogen peroxide such as a 30 percent by weight solution and aqueous hydrofluoric acid such as 49 percent by weight and adding these solutions to water in an amount to provide the desired percentage of the sulphuric acid, hydrogen peroxide, and hydrofluoric acid.

[0018] The compositions containing the ozone can be prepared by bubbling ozone gas into the aqueous composition containing the desired amounts of sulphuric acid and water, or diffusing ozone gas through a membrane into water and then adding sulphuric acid to the water, or by any other suitable method.

[0019] The etchant compositions of the present invention remove the sidewall polymer residue remaining after the reactive ion etching and with it removes any embedded chlorine. The etchant compositions of the present invention also clean vias of other residues, including, but not limited to, oxygen, carbon, silicon and elements of an underlying conductive material. Furthermore, the etchant compositions of the present invention, at most, only mildly etch the aluminum/copper line. Since hydrofluoric acid is known to etch aluminum/copper, the amounts in the etchant solution must be small. When the amounts of hydrofluoric acid in the claimed etchant solution are kept small (less than about 40 ppm) the potentially detrimental effects of the hydrofluoric acid on aluminum/copper are minimized. In most cases, no evidence of any local etching of the aluminum, even aluminum in the vicinity of tungsten studs, has been observed. The tungsten seems to act as a catalyst in etching aluminum when using the prior art chromic/phosphoric acid bath.

They also can be used to remove and clean residues after chemical-mechanical polishing and other "cleaning" processing steps.

[0020] The etchant compositions of the present invention also result in the formation of a pristine native oxide of aluminum which acts as a passivating layer against subsequent corrosion. For instance, an oxide thickness of about 30 angstroms as measured by Auger Spectroscopy is obtained using an etchant composition at about 35°C containing about 2.0 percent by weight of sulphuric acid, about 1.0 percent by weight of hydrogen peroxide and about 10 ppm of hydrofluoric acid.

[0021] The above disclosed relative amounts of components of the composition tend to prevent redeposition of the polymer residue. This occurs by having the pH of the etchant such that the charges of the zeta potentials of the aluminum oxide species and the silicon oxide surface of the substrate cause a repulsion interaction between the surfaces. The desired pH is ensured by observing the amounts of ingredients mentioned above. The zeta potential reflects the charge induced on a surface caused by the interactions of that surface with the ions in the solution, primarily, hydrogen and hydroxide. At a certain solution pH, the net surface charge will be zero which occurs at about pH 2 to 3 for silica and at about pH 9 to 10 for alumina. When the pH is less than this point of zero charge, the charge on the surface would be positive. For the case of a polymer residue removed in an acid medium, the propensity of redeposition of the residue on either the oxidized aluminum surface or on the silica dielectric material is reduced because all surfaces would have a charge of the same sign with zeta potentials also of the same sign. It should be noted that HF acid in the concentrations employed in the present invention (less than about 100 ppm) do not result in significant changes in the pH of the resulting etchant solution.

[0022] The etchants of the present invention can be used to contact the substrate where the polymer or via residue is to be removed by any known technique, such as dipping in a bath or preferably spraying the composition on the substrate or silicon wafer having the aluminum copper lines thereon. Typically, the composition is sprayed at a temperature of about 25 to about 95°C and preferably at a temperature of about 30 to about 50°C for about 1 to about 8 minutes, typical of which is about 2 minutes. Following this, the wafer can be subjected to a deionized water rinse followed by drying.

[0023] The process of the present invention is also capable of removing chlorine embedded material along with the aluminum/copper sidewall polymer residue. The aluminum/copper profiles achieved by the present invention can be smoother than those in the prior art and are capable of being substantially free of electrochemical or accelerated etching of Al/Cu lines near tungsten studs.

[0024] The following Table 1 illustrates various etch rates of the Al/Cu with the etchant compositions of the present invention. The percentages in Table 1 are volume percents for 98 percent by weight H_2SO_4 and 30 percent by weight of H_2O_2 (remainder is H_20).

TABLE 1

Etch rate of Al/Cu with sulphuric/peroxide			
Etch rate of Al/Cu samples (Gravimetry)			
Sulphuric (percent)	Peroxide (percent)	Etch rate[1] (Angstroms/min)	Temperature °C
2.5	2.5	51/116	35/45
2.5	5.0	57/109	35/45
5.0	2.5	68/148	35/45
5.0	5.0	59/136	35/45
7.5	5.0	78	35
7.5	7.5	77	35

[1] Etch rate increases with temperature

[0025] Table II illustrates various etch rates of the aluminum with 0.5% copper alloy with the etchant compositions of the present invention. The percentages in Table II are volume percents for 98 percent by weight H_2SO_4 and 30 percent by weight of H_2O_2 (remainder is H_20).

TABLE II

Etch rate of Al/Cu with sulphuric/peroxide/hydrofluoric (gravimetry)	
HF (ppm)	Etch Rate (Angstroms/min)
0	18
10	69

TABLE II (continued)

Etch rate of Al/Cu with sulphuric/peroxide/hydrofluoric (gravimetry)	
HF (ppm)	Etch Rate (Angstroms/min)
20	107
30	173

[0026] Etch rates were evaluated by measuring the total Al/Cu etched (gravimetry) with 30 minute process time at about 35°C. The solution employed to develop Table II comprised about 9 percent by weight of sulphuric acid, 4 percent by weight of hydrogen peroxide with hydrofluoric acid, with the addition of the amounts of hydrofluoric acid shown in the first column and with the remainder of the solution comprising water.

[0027] The percentages shown in the above in Table 1 and Table II are exemplary only and others within the scope of the invention can likewise be employed. The measured etch rates were evaluated by averaging the total amount of Al-Cu etched over the process time. In this disclosure there are shown and described only the preferred embodiments of the invention, but, as aforementioned, it is to be understood that the invention is capable of use in various combinations and environments and is capable of changes or modifications within the scope of the inventive concept as expressed herein.

Claims

1. An etchant composition in an aqueous solution comprising:

   a) about 0.01 to about 15 percent by weight of sulphuric acid;

   b) about 0.1 to about 100 ppm of a fluoride containing compound; and

   c) a member selected from the group consisting of about 0.01 to about 20 percent by weight of hydrogen peroxide and about 1 to about 30 ppm of ozone.

2. An etchant composition as claimed in to claim 1 wherein the fluoride containing compound comprises hydrofluoric acid.

3. An etchant composition as claimed in claim 1 or claim 2 which comprises about 0.01 to about 20 percent by weight of hydrogen peroxide.

4. An etchant composition as claimed in claim 1 or claim 2 which comprises about 1 to about 30 ppm of ozone.

5. An etchant composition as claimed in any preceding claim which comprises about 1 to about 10 percent by weight of sulphuric acid and about 1 to about 10 percent by weight of hydrogen peroxide and about 1 to about 50 ppm of hydrofluoric acid.

6. An etchant composition as claimed in any one of claims 1 to 5 which comprises about 5 percent by weight of sulphuric acid, about 12 percent by weight of hydrogen peroxide and about 10 ppm of hydrofluoric acid.

7. An etchant composition as claimed in any preceding claim which includes deionized water.

8. A method of removing inorganic polymer residue present on a substrate employing the etchant composition as claimed in any preceding claim.

9. A method of removing polymer and via residue from a substrate, which method comprises contacting the substrate with an aqueous solution comprising:

   a) about 0.01 to about 15 percent by weight of sulphuric acid;

   b) about 0.1 to about 100 ppm of a fluoride containing compound; and

c) a member selected from the group consisting of about 0.01 to about 20 percent weight of hydrogen peroxide and about 1 to about 30 ppm of ozone.

10. A method as claimed in claim 8 or claim 9 wherein the fluoride containing compound comprises hydrofluoric acid.

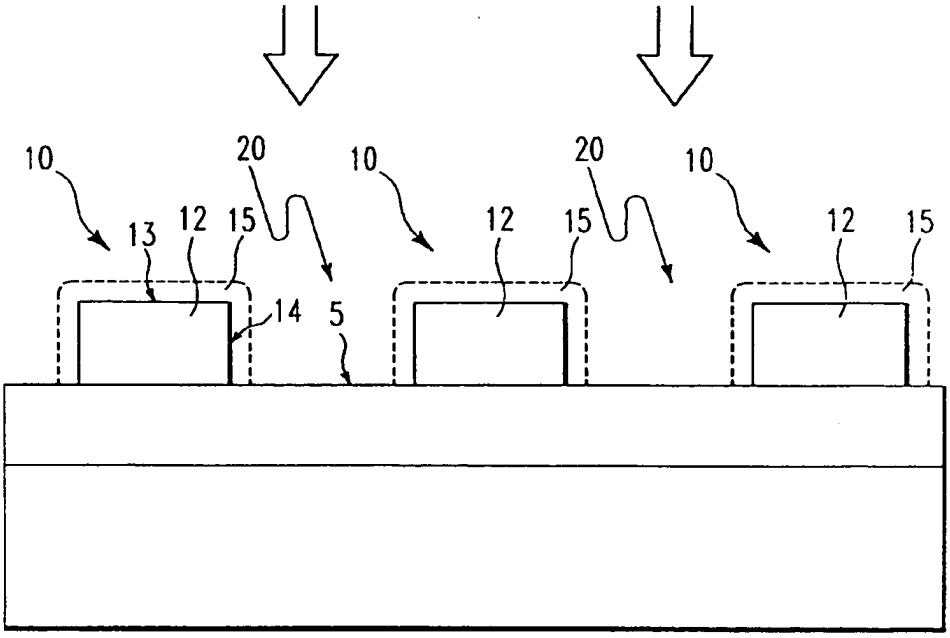
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FIG. 1

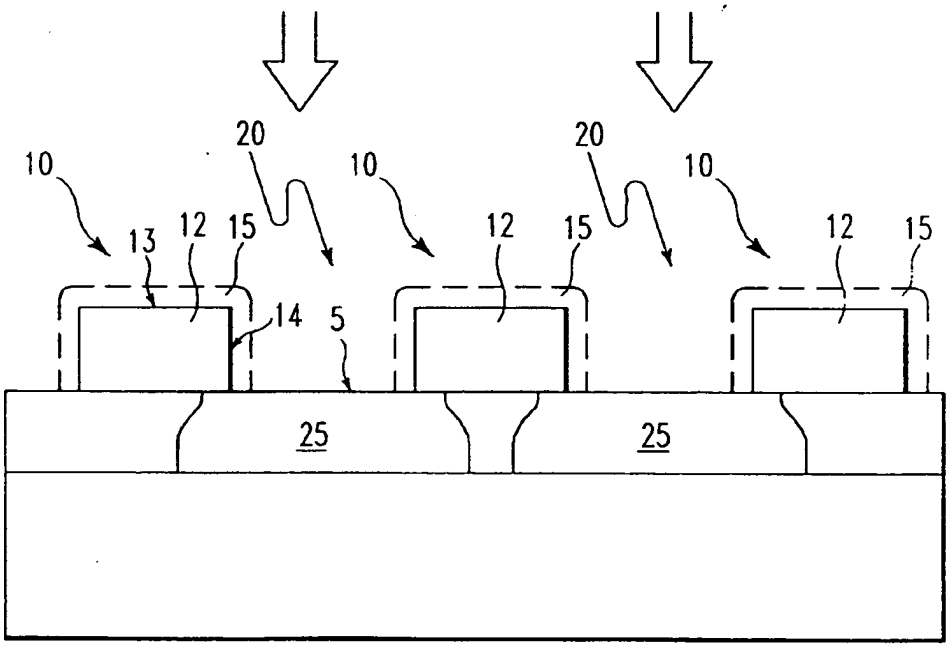
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FIG. 2

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EUROPEAN SEARCH REPORT

Application Number
EP 98 30 8276

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	25 February 1999	Shade, M

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EUROPEAN SEARCH REPORT

Application Number
EP 98 30 8276

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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